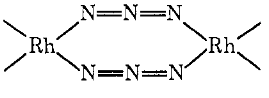
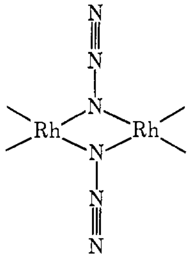
are practically unchanged by varying the coordinated diolefins. It can be seen that the $\nu_{as}(N_3)$ in the $[(CO)_2RhN_3]_2$ dimer is higher than that of the analogous diene derivatives and of other d^8 azido-bridged complexes.[5,7]

For the $[(L_\pi)_2RhN_3]_2$ two structures are possible



A



B

Both structures have D_{2h} symmetry and so cannot be distinguished on the basis of the number of infrared-active vibrations. However, the appearance of ν_s in the ir spectra of the azido-bridged complexes as a medium-strong band strongly supports structure B in which a single atom is bridging.

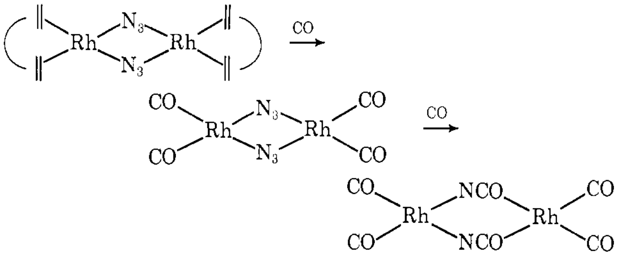
Bridge-Splitting Reactions of the $[(L\pi)_2RhN_3]_2$ Complexes.—To study the reactivity of the dimeric complexes, we have carried out some bridge-splitting reactions with triphenylphosphine and amines.

The reactions of $[(L_\pi)_2RhN_3]_2$ with triphenylphosphine are similar to those observed for the analogous chloro-bridged complexes, the monomeric $[(L_\pi)_2Rh(P(C_6H_5)_3)N_3]$ being obtained. The infrared spectra of these products show that the $\nu_{as}(N_3)$ is lower (~30 cm^{-1}) than that of the corresponding dimeric compounds.

In the case of amines such as pyridine or *p*-toluidine, no reaction occurs even with a large excess of ligand. The attempted preparation of the monomeric compounds (diene)RhN_3(amine) by methathesis from the chloro derivatives was unsuccessful and in fact $[(diene)RhN_3]_2$ was isolated from the reaction of (diene)Rh(amine)Cl with N_3^-. This behavior reflects the greater stability of the azido-bridged complexes with respect to the corresponding chloro compounds.

Reactions of $[(L_\pi)_2RhN_3]_2$ with CO.—It has been shown[14,15] that azido complexes of the types $(CO)ML_2N_3$ (M = Rh, Ir) and $M(N_3)_2L_2$ (M = Pd, Pt) react with carbon monoxide to give the corresponding cyanato complexes. A similar reaction occurs with the $[(L_\pi)_2RhN_3]_2$ complexes. These compounds and the diene derivatives react with carbon monoxide in dichloromethane at room temperature to give the cyanato-bridged complex $[(CO)_2Rh(NCO)]_2$. The cyanato-bridged compound has been characterized by elemental analysis (Table I) and its ir spectrum (Table II). It dissolves in chlorinated solvents giving yellow solutions. Its infrared spectrum in cyclohexane solution shows bands at 2185 (s) and 1303 cm^{-1} (m) attributed to ν_{as}(NCO) and ν_s(NCO), respectively.[17]

The following scheme is likely for the reaction of $[(diene)RhN_3]_2$ with carbon monoxide



This is in agreement with the fact that the overall reaction is complete after 1 day, whereas it is known that the displacement of the olefin by CO in complexes of the type (diene)RhLCl is fast (~1 hr).[18] Moreover, an ir spectrum of the reaction mixture taken after 3 hr shows ν_{as}(NCO) and $\nu_{as}(N_3)$ at 2185 and 2092 cm^{-1}, respectively, indicating that no olefin derivative is present.

The method reported in this paper for the preparations of the azido- and cyanato-bridged complexes of Rh^I appears to be of general applicability, although it was not possible to isolate $[(P(C_6H_5)_3)_2RhN_3]_2$. The preparation of other azido-bridged complexes of Pt^{II} and Pd^{II} is in progress and will be reported in a further publication.

Acknowledgments.—This work was supported by the Italian National Council of Research (CNR, Rome).

[17] J. Nelson and S. M. Nelson, *J. Chem. Soc. A*, 1597 (1969).

[18] J. W. Kang and P. M. Maitlis, *Can. J. Chem.*, **46**, 897 (1968).

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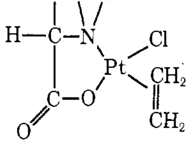
Platinum(II)-Olefin Complexes Containing Amino Acids. I. Preparation and Structure of Several Platinum(II)-Ethylene Complexes with Amino Acids[1]

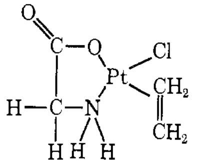
BY JUNNOSUKE FUJITA, KAZUO KONYA,
AND KAZUO NAKAMOTO*

Received June 8, 1970

Recently, Kieft and Nakamoto[2] and Panunzi, *et al.*,[3] prepared a novel Pt(II) complex, chloro(glycino)(ethylene)platinum(II), by treating Zeise's salt with glycine. They proposed structure I in which the nitrogen



I (N-trans isomer)



II (O-trans isomer)

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* To whom correspondence should be addressed at Marquette University.

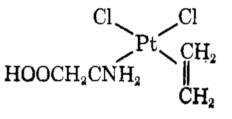
[1] This work was supported by a Petroleum Research Fund unrestricted research grant (3318-C3,5) administered by the American Chemical Society.

[2] J. A. Kieft and K. Nakamoto, *J. Inorg. Nucl. Chem.*, **30**, 3103 (1968).

[3] A. Panunzi, R. Palumbo, C. Pedone, and G. Paiaro, *J. Organometal. Chem.*, **5**, 586 (1966).

atom of the chelated glycine anion is coordinated to the platinum atom in the position trans to ethylene (N-trans isomer). This structure was preferred to structure II (O-trans isomer) because the chlorine atom trans to ethylene of Zeise's salt is labile due to the strong trans effect of ethylene, and the Pt atom prefers to form a bond with the nitrogen rather than the oxygen atom of the glycino anion.

In order to prove the validity of structure I, it is desirable to prepare its O-trans isomer containing ethylene and glycine (structure II). The O-trans isomer may be obtained from the hydrolysis of *cis*-dichloro(ethylene)(glycine)platinum(II)



III

We have, therefore, prepared this compound from potassium dichloro(glycino)platinate(II). However, an attempt to isolate the O-trans isomer (structure II) was not successful because of its high solubility in water. Hence, we prepared its L-alanine analog through the same process. In this case, the O-trans isomer was successfully isolated from the solution.

This paper reports the preparation of several platinum(II) complexes containing ethylene and an amino acid and their geometrical structures as determined by ultraviolet and infrared spectroscopy.

Experimental Section

Preparation of Compounds.[4] (1) ***cis*-$PtCl_2(C_2H_4)(glyH)\cdot H_2O$**.—A 0.01-mol sample of $K[PtCl_2(gly)]$[5a] was dissolved in a minimum amount of 2 *M* HCl, and ethylene was passed through the solution.[5b] After 3 days, the solution was dried *in vacuo* over NaOH and concentrated H_2SO_4. The crude product thus obtained was dissolved in 20 ml of chloroform or acetone to remove KCl. The filtrate was dried *in vacuo*, and the residue was dissolved in a minimum amount of acetone. About 20 ml of ether was added to this solution. After 3 days, pale yellow crystals were formed. They were filtered, washed with ether, and then dried over P_2O_5; mp 118°. *Anal.* Calcd for $C_4H_{11}Cl_2NO_3Pt$: C, 12.41; H, 2.86; N, 3.62. Found: C, 12.88; H, 2.30; N, 3.55.

(2) ***cis*-$PtCl_2(C_2H_4)(sarH)$**.—The same method as (1) was used with $K[PtCl_2(sar)]$ as the starting material. In this case, *cis*-$PtCl_2(C_2H_4)(sarH)$ crystallized during the reaction with ethylene. The product was dissolved in acetone and precipitated by adding ether; mp 125°. *Anal.* Calcd for $C_5H_{11}Cl_2NO_2Pt$: C, 15.67; H, 2.90; N, 3.66. Found: C, 15.94; H, 3.05; N, 3.74.

(3) **$PtCl(C_2H_4)$(L-ala) (N-Trans Isomer)**.—This complex was prepared by modifying the method of Kieft and Nakamoto.[2] Zeise's salt (0.01 mol) and L-alanine (0.01 mol) were suspended in 30 ml of water and cooled in an ice bath. To this solution was added the calculated amount of a $KHCO_3$ solution with stirring. After L-alanine was dissolved completely, the solution was warmed at 40° for 4–5 min. Pale yellow crystals were formed by cooling in an ice bath. The crystals were filtered and washed with a small amount of cold water, ethanol, and ether; dec pt 132°. *Anal.* Calcd for $C_5H_{10}ClNO_2Pt$: C, 17.32; H, 2.91; N, 4.04. Found: C, 16.87; H, 3.05; N, 4.16.

(4) **$PtCl(C_2H_4)$(L-ala) (O-Trans Isomer)**.—$K[PtCl_2$(L-ala)] was dissolved in a small amount of concentrated HCl, and the solution was dried *in vacuo* over NaOH and concentrated H_2SO_4. The yellow residue ($K[PtCl_3$(L-alaH)]) thus obtained was dissolved in 2 *N* HCl, and ethylene was passed through the solution for 3 days.[5b] During the course of the reaction, the color of the solution changed from yellow-brown to pale yellow. After filtering, the solution was dried *in vacuo* and the residue was dissolved in acetone and filtered to remove KCl. The filtrate was dried *in vacuo*, and the residue was recrystallized from water; dec pt 155°. *Anal.* Calcd for $C_5H_{10}ClNO_2Pt$: C, 17.32; H, 2.91; N, 4.04. Found: C, 17.61; H, 2.79; N, 4.04.

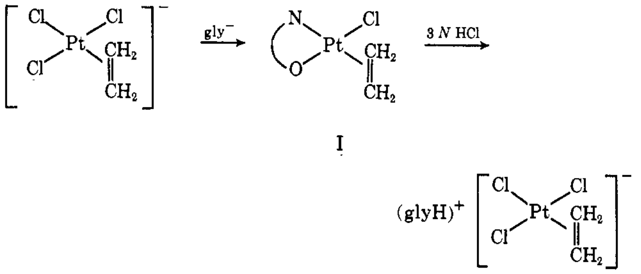
(5) **$PtCl(C_2H_4)$(L-prol) (N-Trans Isomer)**.—This complex was prepared by method (3) except L-proline was used instead of L-alanine; dec pt, 152°. *Anal.* Calcd for $C_7H_{11}ClNO_2Pt$: C, 22.56; H, 2.97; N, 3.67. Found: C, 22.88; H, 3.30; N, 3.67.

(6) **$(glyH)[PtCl_3(C_2H_4)]$**.—This complex was obtained by dissolving $PtCl(C_2H_4)(gly)$ (N-trans isomer)[2] in a small amount of HCl and drying the solutio *in vacuo*. *Anal.* Calcd for $C_4H_{10}Cl_3NO_2Pt$: C, 11.85; H, 2.49; N, 3.45. Found: C, 12.48; H, 3.13; N, 3.13.

Spectral Measurements.—A Beckman IR-12 infrared spectrophotometer was employed to measure the infrared spectra in the 4000–250-cm^{-1} region. The spectra were obtained using the KBr-disk method. The uv spectra were obtained using a Hitachi 124 recording spectrophotometer. All spectral measurements were made at room temperature.

Results and Discussion

As stated previously, Kieft and Nakamoto[2] prepared *N-trans*-$PtCl(C_2H_4)$(gly) by the direct reaction of Zeise's anion with the glycino anion

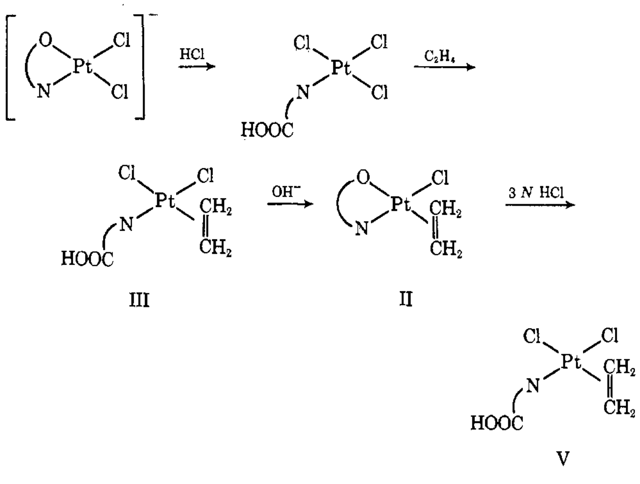


I

IV

They proposed the N-trans structure (structure I) because of the reasons mentioned previously. The N-trans isomers of analogous L-alanino and L-prolino complexes have been prepared by the same method as that used for the glycino complex.

The O-trans isomer was prepared through the synthetic route



III

II

V

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[4] Abbreviations: gly, glycino anion; sar, sarcosino anion; L-ala, L-alanino anion; L-prol, L-prolino anion.

[5] (a) J. A. Kieft and K. Nakamoto, *J. Inorg. Nucl. Chem.*, **29**, 2561 (1967); (b) J. Chatt and M. L. Searle, *Inorg. Syn.*, **5**, 210 (1957).

At the second step, ethylene enters a position which is trans to the Cl atom rather than to the NH_2 group of the amino acid anion, since the order of trans effect is Cl > NH_2. Once the *cis*-dichloro complex (III) is obtained, the O-trans isomer (II) can be derived from it through hydrolysis. We have succeeded in the preparation of the *cis*-dichloro complexes containing glycine, L-alanine, and sarcosine. However, the corresponding O-trans isomers were not isolated for the sarcosine and glycine complexes due to their high solubility in aqueous solution.

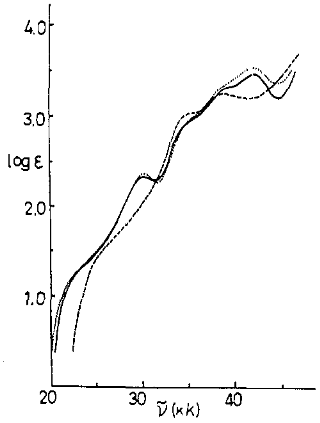

Figure 1.—Absorption spectra of *N-trans*-$PtCl(C_2H_4)$(L-ala) (-----) in H_2O, *N-trans*-$PtCl(C_2H_4)$(L-ala) (——), and $K[PtCl_3(C_2H_4)]$ (......) in 3 *N* HCl.

Uv Spectra.—As is shown in Figure 1, the uv spectrum of *N-trans*-$PtCl(C_2H_4)$(L-ala) in 3 *N* HCl is almost identical with that of Zeise's anion. This result suggests that the L-alanino ligand in this compound is completely dissociated in 3 *N* HCl solution to give the $PtCl_3(C_2H_4)^-$ ion, as is shown in the first reaction scheme. The strong trans effect of ethylene is responsible for the cleavage of the Pt–N bond trans to it. In fact, (glyH)$[PtCl_3(C_2H_4)]$ was isolated from a 3 *N* HCl solution of *N-trans*-$PtCl(C_2H_4)$(gly).

Figure 2 shows that the uv spectrum of *O-trans*-$PtCl(C_2H_4)$(L-ala) in 3 *N* HCl is almost identical with that of *cis*-$PtCl_2(C_2H_4)$(glyH) in the same solvent. This result indicates that the Pt–O bond of the O-trans isomer is cleaved due to the strong trans effect of ethylene but its Pt–N bond remains intact because it is trans to chlorine. Thus, the present uv study supports the validity of the N-trans and O-trans structures proposed for the two isomers of $PtCl(C_2H_4)$(L-ala).

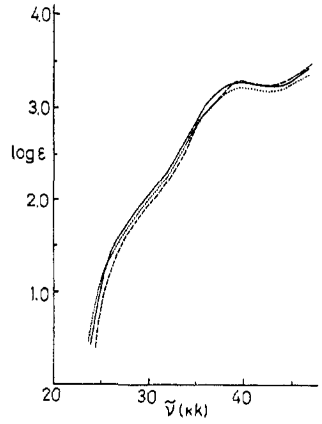

Figure 2.—Absorption spectra of *O-trans*-$PtCl(C_2H_4)$(L-ala) (-----) in H_2O, *O-trans*-$PtCl(C_2H_4)$(L-ala) (——), and *cis*-$PtCl_2(C_2H_4)$(glyH) (......) in 3*N* HCl.

Infrared Spectra.—The cis structures of the $PtCl_2(C_2H_4)$(amH) type of complexes (am = gly, sar, and L-ala) are supported by the appearance of two strong Pt–Cl stretching bands in the region from 350 to 300 cm^{-1}.[6] These compounds also exhibit strong COOH bands of un-ionized amino acids near 1720 cm^{-1} which are characteristic of the unidentate coordination.[5a]

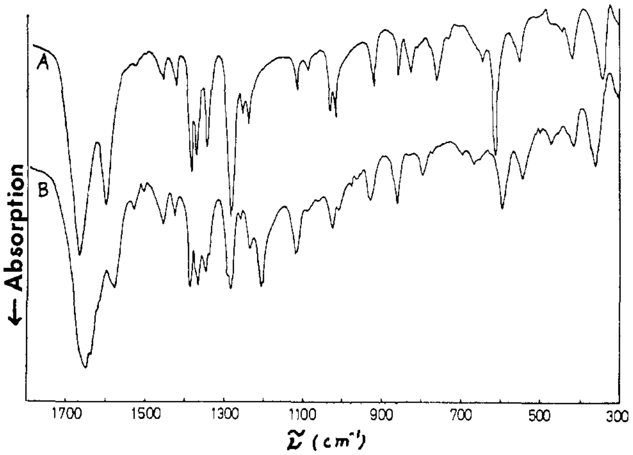

Figure 3.—Infrared spectra of (A) O-trans isomer and (B) N-trans isomer of $PtCl(C_2H_4)$(L-ala).

Figure 3 shows that the spectra of the N-trans and O-trans isomers of $PtCl(C_2H_4)$(L-ala) are essentially similar in the whole frequency region. They can be distinguished, however, by comparing the detailed features of the spectra. It is interesting to note that the Pt–Cl stretching frequency of the O-trans isomer (340 cm^{-1}) is definitely lower than that of the N-trans isomer (360 cm^{-1}). This is because the Pt–Cl bond of the O-trans isomer is weaker than that of the N-trans isomer since the trans effect of the NH_2 group in the former is stronger than that of the COO^- group in the latter. Thus, our ir study again confirms the proposed N-trans and O-trans structures for the two isomers of $PtCl(C_2H_4)$(L-ala) prepared in this investigation.

(6) D. M. Adams, "Metal-Ligand and Related Vibrations," Arnold, London, 1967, p 75.

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Perfluorodimethyl Sulfoxide and Bis(trifluoromethyl)sulfur Difluoride

BY EDWARD W. LAWLESS

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Perfluorodimethyl sulfoxide, $(CF_3)_2SO$, has recently been synthesized in this laboratory and is believed to